Spaced-Confined Capsule Catalysts with Tunable Micro-Environments for Efficient CO2 Conversion

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Abstract

CO2 as a greenhouse gas causes a series of issues, and catalytic utilization of CO2 to fuels is a favorable strategy. Herein, we report the discovery in CO2 hydrogenation reaction where C5+ yield can be evidently improved by encapsulating ZnFe2O4 inside ZSM-5, in which the micro-environments of core-shell components can be tuned. For the ZnFe2O4, the K promoter makes the Fe-C structure more electron deficient than the Na, which contributes to the formation of long-chain olefins. ZSM-5 with K or Ce modification presents enhanced adsorption ability of alkene, then promoting aromatization and isomerization reactions of alkenes. Compared with Ce, K-ZSM-5 contributes to isomerization rather than aromatization, forming more isoparaffins. In this work, regulating the microenvironment of capsule catalysts provides a new idea for the design of efficient tandem catalysts, and expands the ability of hybrid catalysts against other catalysts, thus presenting an excellent catalytic efficiency for CO2 upgrading.

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ABSTRACT

CO_2as a greenhouse gas causes a series of issues, and catalytic utilization of CO_2 to fuels is a favorable strategy. Herein, we report the discovery in CO_2 hydrogenation reaction where C_{5+} yield can be evidently improved by encapsulating $ZnFe_2O_4$ inside ZSM-5, in which the micro-environments of core-shell components can be tuned. For the $ZnFe_2O_4$, the K promoter makes the Fe-C structure more electron deficient than the Na, which contributes to the formation of long-chain olefins. ZSM-5 with K or Ce modification presents enhanced

adsorption ability of alkene, then promoting aromatization and isomerization reactions of alkenes. Compared with Ce, K-ZSM-5 contributes to isomerization rather than aromatization, forming more isoparaffins. In this work, regulating the microenvironment of capsule catalysts provides a new idea for the design of efficient tandem catalysts, and expands the ability of hybrid catalysts against other catalysts, thus presenting an excellent catalytic efficiency for CO_2 upgrading.

Keywords

Capsule catalyst; CO_2 hydrogenation; Zeolite; Tunable micro-environments; Olefins

1. INTRODUCTION

Since nearly two centuries, extensive use of carbon-based fossil energy sources such as coal, oil and natural gas has rapidly promoted the development of human economy and society.[1-4] The widespread use of fossil fuels has led to rising concentrations of CO_2 in the atmosphere, which brings about prominent problems such as the destruction of the ecological balance and global warming.[5-7] As an easily available source of carbon in nature, the efficient conversion of CO_2 into industrial raw materials has attracted the attention of many researchers.[6,8] The difficulties of the conversion from CO_2 to hydrocarbon cause from that the CO_2 is a stable chemical substance demanding high energy to break C-O bonding barrier and the C-C coupling follows the Anderson-Schulz-Flory (ASF) distribution law which limits selectivity of the target products.[9]

The conversion from CO_2 to hydrocarbons is mainly achieved by two ways: one is the reaction process of methanol as an intermediate product, and another is achieved by a modified Fischer-Tropsch (FT) reaction.[3,10-13] In a methanol-mediated route, mixtures of CO_2 and H_2 have been reacted to form methanol intermediates, followed by dehydration to hydrocarbons over a zeolite.[14] However, the process suffers from many problems, in particular, high CO by-product selectivity, low catalytic activity and poor stability, which hinder its commercialization.[15-17] In terms of FTS route, CO_2 is firstly transformed into CO via reverse water-gas shift (RWGS) reaction and then the formed CO is subsequently converted to hydrocarbons.[18-20] It has been found that the reactivities of Ni, Ru, Co, Cu and Fe metals are high, and widely used to catalyze the hydrogenation of CO_2.[7,10,21,22] Especially, Fe-based can *in-situ* form Fe_3O_4 and Fe_xC_y active phase, synergistically catalyzing RWGS and carbon chain propagation.[10,21,23,24] Yet despite, the ASF distribution law is not conducive to attaining a high selectivity of target product in single iron-based catalysts. Generally, CO_2 adsorption occurs on basic sites, thus alkali metal such as K and Na are applied as promoter to enhance the adsorption capability and/or activation ability of CO_2.[22,25-28] The alkali metal can improve the electronic environment of iron, which increases the surface basicity and results in an improvement in CO_2adsorption. This method improves the conversion of CO_2indeed, but the problem of low liquid hydrocarbon selectivity still remains (less than 55%).[26,27,29] Furthermore, the incorporation of second active metal (Co or Cu) also exhibits a facilitating effect by pulling RWGS or chain propagation reaction. The corresponding catalyst also achieves a high selectivity of liquid hydrocarbon or yield.[30-32]

In addition to the systems mentioned above, coupling Fe-based catalysts and zeolite is an alternative prospective way.[22,33-35]It is an effective chemical process intensification strategy by coupling multiple consecutive chemical reactions in a vessel/catalyst under similar or identical conditions.[10,33,35] ZSM-5 have been employed extensively for the isomerization reactions owing to their unique steric properties such as MFI topology, porosity, and acidity.[21,36-38] Wei et al. reported a Na-Fe_3O_4/HZSM-5 for directly converting CO_2 to gasoline-range hydrocarbons. Three types of active sites (Fe_3O_4, Fe_5C_2 and acid sites) achieve a synergetic catalytic conversion of CO_2 to gasoline.[39,40] Noreen et al. designed a dual-bed reaction with SAPO-11 and ZSM-5 coupled individually with the NaFe catalyst, obtaining a high octane gasoline fuel.[41]Since zeolite catalysts can directly participate in the catalytic reaction process, CO_2 hydrogenation process can be tuned by controlling the acidity of zeolite. Brønsted-acid site of the zeolite catalyst is derived from the tri-coordinated Si-OH-Al bridge hydroxyl groups on the skeleton and in the pores. The acid site of the zeolite affects the process of its proton transfer or acceptance of electron pairs, thereby affecting its catalytic activity.[42,43]In previous study, we found that H-ZSM-5 treated by metal nitrate solutions presents different surface acid properties, and the elimination of strong acids is conducive to the formation of high-carbon hydrocarbons.[18,44]

Similarly, through the precise regulation of zeolite acidity and pore size, it is regarded as an efficient tool for achieving a promoting effect on the selectivity of the gasoline hydrocarbon product.[41,45-47]

Despite olefins undergo reactions such as polymerization, isomerization, disproportionation, etc. over the acid site of zeolite, there has been no related report mentioning that how the types of olefins species will impact the selectivity of products on zeolite for CO_2hydrogenation. In addition, most of these traditional iron-zeolite composite catalysts are generally prepared by physical mixing or impregnating, which results in uneven distribution of active sites or no preferred order of reactions.[48-50] Contrary to a catalyst fabricated by physical mixing, a composite with core-shell structure displays distinct advantages. Constructing a catalyst in which the core catalyst produces different types of alkenes and the zeolite has different acidity (that is, the core-shell micro-environment regulation of the catalyst) has potential heuristic significance for the utilization of CO_2.

Herein, based on rotation coating method, the capsule catalysts are fabricated with alkali metal modified spinel-like $ZnFe_2O_4$ as the core and an outer encapsulated ZSM-5 (molar ratio [?] 25-30) as the shell. During the reaction process, olefins are formed on spinel-like $ZnFe_2O_4$, then the olefins will migrate on H-ZSM-5 shell proceeding catalytic reforming to high carbon hydrocarbons over acidic sites, in which K-modified $ZnFe_2O_4$ have a higher heavy olefins selectivity than Na-modified $ZnFe_2O_4$. H-ZSM-5 treated by different ions (K and Ce) exchange exhibits enhanced olefins adsorption capacity, further promoting the formation of gasoline-range hydrocarbons. K-ZSM-5 contributes to the isomerization reaction, while Ce-ZSM-5 promotes the aromatization reaction.

2. EXPERIMENTAL SECTION

2.1. Chemical. All chemicals were purchased from chemical companies and used without further purification: Iron (III) nitrate nonahydrate (Fe $(NO_3)_3$*$9H_2O$, AR 98.5%, Sinopharm Chemical Reagent Co., Ltd. China), Zinc nitrate hexahydrate (Zn $(NO_3)_2$*$6H_2O$), AR 99%, Sinopharm Chemical Reagent Co., Ltd. China), Sodium hydroxide (NaOH, AR, 96%, DAMAO CHEMICAL REAGENT FACTORY. China), Potassium hydroxide (KOH, AR, 85%, Sinopharm Chemical Reagent Co., Ltd. China), ZSM-5 ($(SiO_2)_x(Al_2O_3)_y$, SiO_2/Al_2O_3 (mole ratio) [?] 25-30, Shanghai MackLin Biochemical Technology Co., Ltd, China), LUDOX$^{(r)}$SM Colloidal Silica (30 wt%, Grace Trading (Shanghai) Co., Ltd. China), Potassium nitrate (KNO_3, > 99.0%, Sinopharm Chemical Reagent Co., Ltd. China), Cerium nitrate hexahydrate ($Ce(NO_3)_3$*$6H_2O$, AR, 99.5%, Shanghai MackLin Biochemical Technology Co., Ltd, China), were selected to fabricate the samples.

2.2 . Synthesis of $ZnFe_2O_4$. The synthesis of spinel-like $ZnFe_2O_4$ catalyst was referred to our previous report by a solvent-thermal method. Typically, 2.02g iron (III) nitrate hexahydrate and 0.74g zinc nitrate hexahydrate (Zn: Fe=1: 2 molar radio) were dissolved in distilled water (40 mL), and 0.1 mol NaOH was added into aqueous solutions to ensure alkaline solution. Transferring the solution to a 100 mL Teflon tube being set in a stainless autoclave and placing it in an oven at 180 degC for 8 h for the synthesis reaction. After the product was cooled to ambient temperature, the product was washed with 0.5 L deionized water to control the amount of Na and dried at 60 degC, denoted as Na-$ZnFe_2O_4$. Instead of NaOH with KOH, K-$ZnFe_2O_4$ can be obtained by the same procedure.

2.3. Synthesis of $ZnFe_2O_4$@H-ZSM-5. The $ZnFe_2O_4$@H-ZSM-5 composite catalyst with a core-shell structure coupled modified spinel-like $ZnFe_2O_4$ catalyst and H-ZSM-5 catalyst by spin coated method. Transferring the 0.2 g $ZnFe_2O_4$ catalyst (Na or K) wetted with colloidal silica (30 wt %) into a round-bottom flask. Subsequently, 0.15 g ZSM-5 was added into the flask, and spinning round-bottom flask made H-ZSM-5 and $ZnFe_2O_4$ in intimate contact, forming a composite catalyst with a capsule structure.

2.4. Synthesis of M-ZSM-5 (K, Ce). Surface acid properties of parent H-ZSM-5 zeolite (Si/Al = 25-30) was treatment through different ions-exchange strategies. Prior to treatment, H-ZSM-5 was calcinated at 550 degC to remove adsorbed water molecules. Subsequently, H-ZSM-5 (1.0g) was directly treated by one of nitrate solution of K or Ce ion (100 mL, 0.2 mol/L) at 80 degC for 12 h. The filtered H-ZSM-5 was rinsed several times with plenty of deionized water, and then it was calcined at 550 degC for 5 h. Finally, the obtained products were labelled as M-ZSM-5, in which M stands for the exchanged ion. 1 g K-ZSM-5 was treated in 100ml of NH_3*H_2O (0.2 mol/L) solution at 80 degC for 12 h, to obtain H-ZSM-5*.

2.5. Catalysis evaluation. The catalytic reactions were carried out in a stainless steel fixed-bed reactor. Typically, 0.35 g of composite catalyst (20-40 mesh), M-$ZnFe_2O_4$@M-ZSM-5, was used. Prior to reaction, the catalyst was *in situ* reduced in pure H_2 with 50 mL/min at atmospheric pressure, 400 degC for 6 h. After reduction, the temperature was cooled to 320 degC and the reactant gas with H_2/CO_2 ratio = 3/1 (24.15% CO_2, 71.71% H_2, and 4.14% Ar was employed as an internal standard) was switched into the reactor. The reactions were conducted at 320 degC, 2.0 MPa with a reaction gas flow rate of 20 mL/min.

CO_2 conversion and CO selectivity were analyzed by an online gas chromatograph (GC) using a thermal conductivity detector (TCD, Anhui Chromatographic instrument GC5190). The light hydrocarbons were analyzed by an online GC with a flame ionization detector (FID, Anhui Chromatographic instrument GC5190). N-octane (C_8) as solvent was equipped to capture the heavy hydrocarbons in the effluents, and the products were analyzed by an off-line GC using an FID. The detailed product distribution was calculated as previously reported.

CO_2 conversion, CO selectivity, and hydrocarbon selectivity were calculated on a molar carbon basis:

$$\mathrm{CO_2\ conversion\ (\%)} = \frac{\mathrm{CO_{2\ in}} - \mathrm{CO_{2\ out}}}{\mathrm{CO_{2\ in}}} \times 100\%$$

Where the CO_{2in} and CO_{2out} represent the moles of CO_2 at the inlet and outlet, respectively.

$$\mathrm{CO\ selectivity\ (\%)} = \frac{\mathrm{CO_{\ out}}}{\mathrm{CO_{2\ in}} - \mathrm{CO_{2\ out}}} \times 100\%$$

Where the CO_{out} represent the moles of CO at the outlet.

The selectivity of hydrocarbons (C_i) in total hydrocarbons was obtained by the following formula:

$$\mathrm{C_i\ hydrocarbon\ selectivity\ (C-mol\%)} = \frac{\mathrm{mol\ of\ C_i} \times \mathrm{i}}{\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{mol\ of\ C_i} \times \mathrm{i}}$$

The space-time yield (STY) of C_{5+} hydrocarbons on catalyst was obtioned by the following formula:

$$\mathrm{STY} = \frac{\mathrm{CO_2\ Conversion} \times (1 - \mathrm{CO\ selectivity}) \times \mathrm{C_{5+}hydrocarbon\ selecitivity}}{\mathrm{Catalyst\ mass\ (g)}}$$

2.6. Catalyst Characterization. X-ray diffractometer (SmartLab 9kW) with Cu Kα radiation was used to obtain diffraction patterns. The surface morphologies of the catalysts were investigated using scanning electron microscopy (SEM, Regulus 8230). Transmission electron microscopy (TEM, JEOL JEM-2100F) was used to observe particle size sand distribution at an acceleration voltage of 100 kV. The adsorption behavior of the catalyst was measured by using a Micromeritics AutoChem II Chemisorption Analyzer 2920. AutoChem II analyzer with a thermal conductivity detector (TCD) was used to acquire H_2temperature programmed reduction (H_2-TPR) profiles. A 50 mg sample was first pretreated with He for 1 h at 200 °C. When the temperature was cooled to 50 °C, a 5vol % H_2/Ar gas mixture was supplied to the reactor (30 mL/min). Finally, H_2-TPR profiles were obtained at temperatures ranging from 50 to 700 °C, with a heating rate of 10 °C/min. The same equipment was also used to investigate the CO_2 or NH_3 temperature-programmed desorption (TPD). A 50-mg sample was reduced for 2 h at 400 °C under a H_2 gas flow (30mL/min). The temperature of the catalysts was reduced to 50 °C under a He gas flow (30 mL/min) after reduction. There actor was subsequently filled with a 5% CO_2/He or 5% NH_3/He gas mixture for 1h. He was then inserted into the reactor to remove the physically adsorbed CO_2 or NH_3. The CO_2-TPD and NH_3-TPD profiles were recorded from 50 to 800 °C with a heating rate of 10 °C/min. A Thermo Fischer Scientific ESCALAB 250 Xi instrument with a catalyst pretreatment chamber for altering the gas composition was used to conduct the X-ray photoelectron spectroscopy (XPS) analysis. The XAFS was recorded in table XAFS by Chuang Pu specreation. TG was tested by STA 449C Jupiter®. N_2 physisorption was performed on a ASAP 2460 surface area & pore size analyzer. Prior to texts, the samples were degassed at 200 °C under vacuum conditions. Pyridine adsorption (Py-IR) spectra were recorded with a Thermo IS50 IR spectrometer from Thermo Scientific to the measurement, the sample cell was vacuumed to 10^{-2} Pa at 400 °C for 1 h, and the IR spectra were recorded at 350 °C. The ^{27}Al magic-angle spinning (MAS) NMR was recorded by Bruker Avance 600 AV. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were recorded on a Thermo iS50 FT-IR spectrometer. Before test, the sample was *in situ* reduced at 400 °C under 10 vol% H_2 in Ar (50 mL/min) for 2 h and then switched to He for 15 minutes (50 mL/min). After that, the reaction gas was introduced into the reaction cell for reaction. Finally, at atmospheric and 320 °C, 20 mL/min of mixture gas (24 vol% CO_2, 70 vol% H_2 and 6 vol% Ar) passed through and DRIFT spectra were recorded. To the M-ZSM-5, the sample was *in situ* heating at 320 °C under He for 15 minutes (50 mL/min) and then switched to 20 mL/min of mixture gas as 10 vol% C_3H_6, 90 vol% Ar passed through and DRIFT spectra were recorded at atmospheric, 320 °C. After 10minutes, the mixture gas is stopped and the data is recorded for 20 minutes. Before performing DFT calculations, the composition and structure of the smallest monomer can be determined from literature and experimental results. Based on the determined minimum monomer structure, the smallest monomer is extracted from the polyatomic structure using the super cell builder in CASTEP, a sampling tool provided in the calculation software. This usually requires the setting of periodic boundary conditions and the adjustment of unit cell parameters to ensure the periodicity and compatibility of the smallest monomer structure. Structural optimization: after extracting the smallest monomer structure, structural optimization can be performed in the calculation software to determine the most stable zeolite structure. Then the adsorption energy is calculated.

3. RESULTS AND DISCUSSION

3.1. Characterization of $ZnFe_2O_4$@ZSM-5

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Figure 1. **(a)** XRD patterns of different $ZnFe_2O_4$ catalysts; **(b)** fresh and spent $ZnFe_2O_4$@H-ZSM-5, **(c)**XRD patterns of H-ZSM-5*, K-ZSM-5, La-ZSM-5, Ce-ZSM-5, H-ZSM-5.

The tailor-made capsule catalyst consists of two components: $ZnFe_2O_4$ as core catalyst and ZSM-5 as shell catalyst. XRD patterns of $ZnFe_2O_4$and capsule catalysts were shown in Figure 1. As seen, the main phase of core catalyst is mainly $ZnFe_2O_4$ apart from a small amount of Fe_2O_3, when NaOH as an alkaline thermal-solvent is used. It has been reported that the crystallinity of spinel species increases as the concentration of Na decreases.[28] By contrary, the main Fe phase is $ZnFe_2O_4$ without Fe_2O_3 formation for K-$ZnFe_2O_4$, which indicates that KOH is more conducive to the formation of spinel structure. These phenomena are also consistent with our previous findings about $ZnFe_2O_4$.[24] As drawn in Figure 1b, the $ZnFe_2O_4$@ZSM-5 capsule catalyst and H-ZSM-5 exhibit same diffraction peaks that 2ϑ value of 8.0, 8.9, 23.3, 23.9, and 24.4° (JCPDS 44-0003), suggesting that the MFI topology structure of ZSM-5 zeolite is not destroyed during the encapsulation process of $ZnFe_2O_4$ particles. In addition, XRD spectra of the capsule catalyst have no obvious peaks of Fe phase, indicating that the surface of the nuclear catalyst is completely wrapped by ZSM-5 shell. To verify the structure of the capsule catalyst, the surface morphology of the K-$ZnFe_2O_4$@K-ZSM-5 capsule catalyst was analyzed by SEM in Figure 2d-i. An obvious boundary between the two different components can be observed in the cut section of the capsule catalyst where having different elements distribution profiles in mapping images that Zn, Fe belong to K-$ZnFe_2O_4$ and Si, Al belong to K-ZSM-5 presented. Zn and Fe elemental signals are obviously surrounded by Al and Si elemental from mapping images of the K-$ZnFe_2O_4$@K-ZSM-5 capsule catalyst, which indicates that the $ZnFe_2O_4$ core catalyst is wrapped inside by K-ZSM-5 shell catalyst (Figure 2e). These above results certify that the capsule structure catalyst with the $ZnFe_2O_4$ as core componets uniformly encapsulated by K-ZSM-5 has been successfully synthesized.

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Figure 2. Fe-2p XPS spectra of **(a)** as-prepared and**(b)** spent K-$ZnFe_2O_4$ and Na-$ZnFe_2O_4$; **(c)** the XANES spectra of Fe K-edge in spent $ZnFe_2O_4$;**(d)** SEM images of K-$ZnFe_2O_4$@K-ZSM-5; **(e)** the mapping of all the elements over the above section; **(f)** Fe elemental distribution; **(g)** Zn elemental distribution;**(h)** Al elemental distribution; **(i)** Si elemental distribution.

Compared with as-preapred $ZnFe_2O_4$@ZSM-5 catalyst, phase composition of spent capsule catalyst still remains the MFI structure of ZSM-5, which illustrates that the core-shell structure of the capsule catalyst can maintains excellent physical stability (Figure 1). After reaction, the Zn and Fe in $ZnFe_2O_4$ are transformed into ZnO into Fe_3O_4 and Fe_5C_2, respecively. Thereinto, Zn acts as a structure and electronic promoter can enhance the basicity and thus increases light olefins selectivity. In general, Fe_3O_4, as the active phase for RWGS reaction, promotes the CO_2 molecules into CO intermediates, while the co-existence of Fe_5C_2 as crucial active phase makes the chain propagation to form hydrocarbons. As a consequence, different configuration compositions of Fe_3O_4 and Fe_5C_2 can regulate CO_2conversion performance, leading to clear distinction in activity and selectivity. Besides, the SEM images of Na-$ZnFe_2O_4$ and K-$ZnFe_2O_4$ were shown in Figure S1. As shown in Figure 2b, spent $ZnFe_2O_4$catalysts were performed by a X-ray photoelectron spectroscopy (XPS). The binding energy peaks at 706.4 eV, 710.6 eV, and 712.3 eV are attributed to Fe_5C_2 species, Fe(II), and Fe(III), respecitively. Compared with Fe-2p XPS spectra of as-prepared, highly valenced iron oxide species are converted to carbides and Fe_3O_4, crucial active phases for CO_2 conversion (Figure 2a). It is worth noting that the introduction of Na causes the Fe-C peak shift to a direction with low binding energy. According to the relative content of Fe-2p in different XPS, the spent Na-$ZnFe_2O_4$ have more iron-carbon bonds content than spent K-$ZnFe_2O_4$ (Table S1). HR-TEM images of spent K-$ZnFe_2O_4$ and Na-$ZnFe_2O_4$ catalyst were shown in Figure S2. The 4.64Å and 2.65 Å are belong to Fe_3O_4 (111) and Fe_5C_2 (311), which coincides with the results of XRD and XPS. Obviously, the co-existence of Fe_3O_4 and Fe_5C_2 together push the reaction forward. The morphologies and structures of the core Fe-based catalyst before and after the reaction were also explored. After reaction, the structure of bulk $ZnFe_2O_4$ present uniform dispersion of small particles, assigning to the dynamic transformation of $ZnFe_2O_4$ spinel structure (Figure S1). Besides, after K ions exchange, the morphologies and structures of zeolite change slightly (Figure S3). For a zeolite treated by Ce ions, there are a few crystals on the surface of the zeolite (Figure S4). Moreover, TEM images of zeolites with different ions exchange strategies were compared in Figure S5. It can be clearly found that the exchanged metal ions are evenly distributed in the zeolite. Moreover, the content of the exchanged ions in the zeolite is relatively low (Table S2).

Fe K-edge XANES was used to investigate the nature and coordination properties of Fe species in the spent $ZnFe_2O_4$ catalyst under the relevant operating conditions (Figure 2c and S6). The normalized XANES spectra of the Fe K-edge in $ZnFe_2O_4$ are given in Figure 2c; and the data for Fe foil, $ZnFe_2O_4$, Fe_2O_3, Fe_3O_4 and Fe_5C_2 are also presented. In the XANES spectra, the K-$ZnFe_2O_4$ shifts to a higher energy than Na-$ZnFe_2O_4$, illustrating that K promoter is conducive to the transition of Fe phase to a high valence state of Fe species. The introduction of additives can enhance the electronic transition between active phases and raw molecules, and then achieve the regulation of product selectivity during catalytic reactions. In the wavelet detail of spent $ZnFe_2O_4$,the Fe has the same coordination in Figure S6c and S6d. The difference is that the introduction of K promoter lengthens the number of wave vectors and strengthens the degree of transition of the catalyst to Fe-C during the reaction.

Besides, H_2-TPR patterns of as-prepared Na-$ZnFe_2O_4$ and K-$ZnFe_2O_4$ were compared in Figure S7a. Compared with Na modification, the introduction of K promoter is silghtly conducive to the reduction behavior of iron species. Meanwhile, the CO_2-TPD profiles were shown in Figure S7b. It can be found that all the catalysts of K-$ZnFe_2O_4$ and Na-$ZnFe_2O_4$ have obvious weak adsorption and moderate adsorption. K-$ZnFe_2O_4$exhibits a better absorption of CO_2 than Na-$ZnFe_2O_4$, which because of K has a stronger adsorption capacity for CO_2 than Na or more $ZnFe_2O_4$ phases, which will adsorb more CO_2 than single Fe_2O_3phase. It demonstrates that K-$ZnFe_2O_4$have a high active capability for CO_2 conversion. K-$ZnFe_2O_4$ also exhibits a better absorption of CO than Na-$ZnFe_2O_4$ (Figure S7c).

3.2. Catalytic performance of $ZnFe_2O_4$@ZSM-5

The results of catalytic performances were presented in Figure 3a and Table S3. Na-$ZnFe_2O_4$ catalyst mainly produces C_2-C_4 olefins, in which CH_4 selectivity is 16.6%, C_2-C_4 selectivity is 53.3% and C_{5+} selectivity reaches 30.1% at a CO_2conversion of 28.3%. When K promoter is introduced, C_{5+}selectivity increases from 30.1% to 49.2%, in which CH_4 is 11.0%, C_2-C_4selectivity is 39.8% at a CO_2 conversion of 32.7%. In our previous reports, we found that Na-modified $ZnFe_2O_4$ catalyst facilitates the formation of low-carbon olefins, while K-modification one facilitates the formation of high-carbon hydrocarbons.[24] Based on the above discussion (Figure 2b, 2c, and S7), the performance difference is due to the improved adsorption capacity of CO_2modified with K promoter and the Fe-C structure of carbides more electron deficient. After encapsulation by H-ZSM-5 zeolite shell, the conversion of C_2-C_4 olefins selectivity decrease, whereas the selectivities of CO and CH_4slightly increase. After Ce ions exchange, C_{5+}selectivity of K-$ZnFe_2O_4$@Ce-ZSM-5 increases from 47.8% to 59.9%. Meanwhile, the C_2-C_4 olefins decreased profoundly than the parent H-ZSM-5 (Figure 3a). With the treatment of K, the performance difference between K and Ce modification are obvious. The selectivity of C_{5+} hydrocarbon climbs to 71.7% from 59.9%, producing more liquid fuels than Ce ions treatment. It indicates that changing the microenvironment of the zeolite catalysts by ions exchange is a feasible strategy for regulating products distribution. Catalytic stability of the K-$ZnFe_2O_4$@K-ZSM-5 catalyst was investigated and depicted in Figure 3b. As seen, the catalyst exhibits a benign stability during the 80h reaction period. Liquid hydrocarbons selectivity (C_{5+}) maintains above 70%, and CO_2 conversion as well as un-desired CO byproduct almost keep stable. Comparing with other metal oxide/zeolite composite catalysts, the designed K-$ZnFe_2O_4$@K-ZSM-5 catalyst present a record-breaking C_{5+}-yield based on per gram catalyst (Figure S8 and Table S4). It indicates that the capsule catalyst K-$ZnFe_2O_4$@K-ZSM-5 is a promising catalyst for efficiently catalyzing CO_2 hydrogenation to liquid fuels.

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Figure 3. **(a)** Catalytic performances over different catalysts;**(b)** the catalytic stability of K-$ZnFe_2O_4$@K-ZSM-5 catalyst; **(c)**detailed hydrocarbon distribution over bi-functional catalysts with different ions-exchange strategies for zeolites (K-$ZnFe_2O_4$, K-$ZnFe_2O_4$@H-ZSM5, K-$ZnFe_2O_4$@Ce-ZSM-5 and K-$ZnFe_2O_4$@K-ZSM-5); **(d)** effects of contacting manner on catalytic performance. Reaction conditions, $ZnFe_2O_4$ to ZSM-5 is 0.2g to 0.15g, 2.0 MPa, 320 °C, 6000 $mL\cdot g^{-1}\cdot h^{-1}$ for $ZnFe_2O_4$, H_2/CO_2 = 3.

The gasoline-range hydrocarbons refer to high octane number hydrocarbons, e.g. aromatics and isoparaffins as a highly recognized octane contributor. Octane rating on isoparaffins increases with the number of branches, and such multibranched isomers synthesis are preferred in CO_2 conversion. As shown in the Figure 3c, the main product of K-$ZnFe_2O_4$ is olefins-rich product, which occupies 64.8% in all hydrocarbons. After K-$ZnFe_2O_4$ catalyst encapsuled by H-ZSM-5 shell, the selectivity of gasoline hydrocarbons in the product changes slightly. However, for the types of hydrocarbon product, the reduction in the proportion of olefins in all hydrocarbons is obvious, while the selectivity of isoparaffins and aromatics in the gasoline range increases. The effect can be ascirbed to the introduction of ZSM-5, which increases the selectivities of isoparaffins and aromatics with the help of its pore structure and acidic sites. Compared with H-ZSM-5, the selectivity of C_{5+} hydrocarbons increases by 10% with the introduction of Ce. Besides, the proportion of isoparaffins and aromatics still increases in whole C_{5+} hydrocarbons. However, CH_4 selectivity is higher than K-$ZnFe_2O_4$, which maybe because of the diffusion of the hydrocarbon product via a core-shell structure. The products of K-$ZnFe_2O_4$@K-ZSM-5 are aromatics as main component in C_{5+} hydrocarbons (Figure 3c). More importantly, the ratio of isoparaffins to aromatics gradually increases with the change of M-ZSM-5 (from H-ZSM-5 to Ce-ZSM-5 to K-ZSM-5). It supports that the olefins generated on the surface of K-$ZnFe_2O_4$ catalyst undergo polycondensation, isomerization, aromatization reactions through the acidic site of ZSM-5. Meanwhile, comparing the effects of zeolites with different ions modifications on the selectivity of target hydrocabon, verifies that K modified ZSM-5 exhibits evidently promoting effect for the oriented production of C_{5+} hydrocarbons.

Previously, different contacting manners of composite catalysts, such as physical mixing and multiple beds, will influence matching combination between different active sites, which in turn will affect the catalytic performance.[51,52] It has been reported that a catalyst with a core-shell structure can enhance mass and heat transfer during the reaction comparing with one fabricated by physical mixing manner.[49] The effect of contacting manner between K-$ZnFe_2O_4$ and K-ZSM-5 was investigated. Results of different contacting manners including core-shell catalysts, powder mixing, granule mixing, and dual bed were shown and summarized in the Figure 3d and Table S5. As for a powder mixing one (K-$ZnFe_2O_4$ and K-ZSM-5 are physically mixed firstly and then the mixtures are granulated to obtain 20-40 mesh), the selectivity of C_{5+} is only 20.5%. When K-$ZnFe_2O_4$ and K-ZSM-5 are integrated by granule mixing or dual bed, the selectivity of C_{5+}hydrocarbons (about 62%) over both catalysts are evidently higher than physical mixing one, but lower than the capsule catalyst of K-$ZnFe_2O_4$@K-ZSM-5. Evidently, the capsule structure of K-$ZnFe_2O_4$@K-ZSM-5 exhibits an excellent CO_2 hydrogenation performance, especially C_{5+} selectivity. Interestingly, these two kinds contacting manner both have a slight high CO_2conversion than capsule catalyst. It is possible that the direct exposure of the $ZnFe_2O_4$ catalyst to the reaction atmosphere, and the diffusion influence of reaction gases in zeolite pore is reduced, which improves the utilization of reaction gases.

As discussed above, K-$ZnFe_2O_4$ catalyst coated by K-ZSM-5 shell presents an improved peformacne for CO_2 hdyrogenation. Then, the effect of zeolite shell thickness on catalytic performance were further investigated. With the increase of shell thickness, the particle sizes of capusle catalysts increases obviously, which clearly indicates that the core K-$ZnFe_2O_4$ catalyst was coated with more zeolite (Figure S10). When the mass ratio of zeolite to Fe-based catalyst is 1:1, the K-$ZnFe_2O_4$@K-ZSM-5 shows the best performance (Figure 4a and Table S6). With the further increase of zeolite thickness, the selectivity of long-chain hydrocarbon significantly decreases, which can be ascribed to the overcracking of long-chain products (Figure 4b and 4c).

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Figure 4. **(a)** Effects of zeolite shell thickness on K-$ZnFe_2O_4$@K-ZSM-5 catalytic performance;**(b)** Paraffins composition over composite catalysts with different shell thickness; **(c)** Detailed product distribution over composite catalysts with different shell thickness.

TG analysis of spent $ZnFe_2O_4$ and zeolites was shown in Figure S11. The spent K-$ZnFe_2O_4$ have more more obvious degree of carbonization than spent Na-$ZnFe_2O_4$, and the rising curve is the process by which iron-carbon compounds is converted to ferrites. When K-$ZnFe_2O_4$ is coupled with different ZSM-5, there are more iron-carbon compounds on K-ZSM-5 after the reaction, not only carbon deposits in H-ZSM-5. With the introduction of K-ZSM-5, Na-$ZnFe_2O_4$has more carbon deposition resulting in reduced activity, and K-$ZnFe_2O_4$ is not easily sintered.

Among different zeolite treated by K ion exchange startegy, the K-$ZnFe_2O_4$@K-ZSM-5 exhibited an excellent performance of CO_2 hydrogenation. The catalytic performances of K-$ZnFe_2O_4$ coupled with different kinds of K-modified zeolites were shown in Figure S12 and Table S7. The introduction of K-ZSM-5 in composite system displayed the best C_{5+} hydrocarbons selectivity, which indicates that ZSM-5 with K ion exchange promoted the secondary reaction of olefins to form gasoline-range products due to its unique acidic and pore structure.

3.3. Exploration of ZSM-5 acid-catalysed reaction process

By coupling K-$ZnFe_2O_4$ core catalyst with K-ZSM-5 shell catalyst, the selectivity of gasoline hydrocarbons in the product is improved. To confirm the influences of different zeolites on the target product selectivity, it is necessary to measure the intensities and type of acidic sites of zeolites. NH_3-TPD patterns of H-ZSM-5, Ce-ZSM-5, K-ZSM-5 and H-ZSM-5* were shown in the Figure 5a. The surface acidity of ZSM-5 changes obviously after different metal ions modification. After Ce ions exchange, the surface strong acid of ZSM-5 (above 380°C) decreases, but not as significantly as that of K-ZSM-5. Besides, the surface weak acid of K-ZSM-5 also decreases obviously. These phenomena confirm that the introduction of alkali metals causes the change of acidic sites of ZSM-5. However, the acidic sites of H-ZSM-5* is also stronger than unprocessed H-ZSM-5. The purpose of $NH_3 \cdot H_2O$ treatment for K-ZSM-5 is to replace K^+ ions by NH_4^+ ions, and to verify that alkali metal ions are crucial factors leading to the weakening of acidic sites of ZSM-5. Zeolite is composed of SiO_2 and Al_2O_3, which is easily to desiliconize and dealuminum in alkaline solution. N_2adsorption-desorption isotherms and pore distributions (inset) of H-ZSM-5*, K-ZSM-5, Ce-ZSM-5, H-ZSM-5 were shown in Figure S13 and Table S8. Clearly, H-ZSM-5* has a bigger pore volume than H-ZSM-5 with $NH_3 \cdot H_2O$ treatment. According to previous reports, appropriate pore reaming of zeolite was beneficial to improve the selectivity of macromolecular hydrocarbons.[46] It explaines that H-ZSM-5* is more acidic because the specific surface area increases, and the expansion of pores increases the activity of the catalyst (Figure S9). K-ZSM-5 exhibits a same physical adsorption and desorption results with parent H-ZSM-5. These findings verify that the introduction of K ions weakens the acidity of the ZSM-5. Evidently, it is feasible to regulate the selectivity of the product by regulating the acidity and pores of ZSM-5.

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Figure 5. (a) the NH_3-TPD patterns and (b) the pyridine-adsorption Fourier transform infrared (FT-IR) spectra of H-ZSM-5, Ce-ZSM-5, K-ZSM-5 and H-ZSM-5*.

When zeolite is treated with active components such as metal ions or oxides, new Lewis acidity site and active centers can be formed. With alkali metals K and Ce ions introduction, the H^+ ratio in the ZSM-5 skeleton decreases and the strength of the acidic site decreases. By comparing differences in catalytic performance, the decrease in acidic strength increases the catalytic performance of CO_2 hydrogenation (Figure 3 and 5a).[53]Additionally, the pore size distribution and specific surface area of ZSM-5 change slightly after ions exchange (Figure S13). This phenomenon can be ascribed that alkali metal ions occupy a larger space in the pores than H^+. The acid properties of M-ZSM-5 are further investigated by pyridine-adsorption FT-IR spectra (Figure 5b and Table S9). It is widely accepted that the Bronsted acid sites play a dominant role in isomerization, cracking, and aromatization reactions.[53] As shown in the Figure 5b, the band at 1545 cm^{-1} is ascribed to Bronsted acid sites formed by the framework Al species, while the band at 1456 $cm^{-1}$is related to the Lewis acid sites formed by the extra framework Al species. Compared to H-ZSM-5, the intensity of the band at 1545cm^{-1} decreases obviously with the introduction of alkali metals. At about 1456 cm^{-1}, the intensity of Lewis acid site increases slightly. The variation is same as the result of NH_3-TPD, and illustrate that the substitution of the skeleton Al by other metal ions led to a decrease in Brönsted acid and an increase in Lewis acid site. From SEM and TEM images of the ZSM-5, it is observed that crystals appear on the surfgureace of ZSM-5 after the introduction of Ce, and Ce-ZSM-5 has large amounts of metal particles that are significantly different from H-ZSM-5 (Figure S3-S5). Besides, the Al coordination of zeolite determined by ^{27}Al magic-angle spinning (MAS) NMR is shown in Figure S14 and Table S10. The percentage of extraframework Al increases (Al^{EF}, at 0 ppm), while that of the framework Al decreases (Al^{F}, at 55 ppm).[16,46] The K-ZSM-5 and parent H-ZSM-5 have the same proportion of Al^{F}, which indicates that K ions weaken the acidic site strength by weakening Si-OH-Al. Meanwhile, the Ce ions occupies a large number positions of extraframework Al, resulting in a larger proportion of Al^{F}, but it still present weaker acidic strength than H-ZSM-5.

CO_2 hydrogenation behaviors over K-$ZnFe_2O_4$, K-$ZnFe_2O_4$@H-ZSM5, K-$ZnFe_2O_4$@Ce-ZSM-5, and K-$ZnFe_2O_4$@K-ZSM-5 were further studied by *in situ* diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. As illustrated in Figure 6a, the absorption intensity in the region between 3800 cm^{-1} and 3500 cm^{-1} continues to increase for K-$ZnFe_2O_4$, which corresponds to the hydroxyl vibrational bands belonging to H_2O. The absorption intensity in the region from 3000 cm^{-1} to 2940 cm^{-1} gradually decreases, which usually corresponds to the -CH_2. The absorption peaks at wavenumber less than 3000 cm^{-1} shift to higher wavenumber (>3000 cm^{-1}) with time, indicating that a component shift from saturated C-H bonds to unsaturated C-H bonds. Besides, absorption peaks located at 1680 cm^{-1} to 1500 cm^{-1}, and about 1000 cm^{-1} could be attributed to the

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Figure 6. The *in situ* DRIFT spectra of **(a)**K-$ZnFe_2O_4$, **(b)**K-$ZnFe_2O_4$@K-ZSM5 for CO_2hydrogenation; **(c)** H-ZSM5, **(d)** K-ZSM-5 in C_3H_6 atmosphere (0.1 MPa, 320 °C, 20 mL min^{-1}).

double-bond telescopic vibration of the olefins C=C. It indicates that the presence of olefins in the products is produced over the surface of K-$ZnFe_2O_4$ (**Figure 3a**).

When ZSM-5 is introduced, C=C bond of olefins telescopic vibration absorption peak at 1680-1500 cm^{-1} significantly decreases, replacing by infrared absorption peaks at about 1000 cm^{-1} wavenumber, which are attributed to the off-plane bending vibrations of aromatic compounds different from olefins (Figure 6b and S15). The infrared absorption spectra of aromatic compounds are more pronounced in the K-$ZnFe_2O_4$@Ce-ZSM-5 and K-$ZnFe_2O_4$@K-ZSM-5 (Figure S15). Besides, there are many bending vibrations of -CH_3 unlike other catalysts, which are multiple methyl groups linked to the same carbon atom. For the K-$ZnFe_2O_4$@K-ZSM-5, more bending vibrations of -CH_3 appear than the utilization of other zeolite catalysts, which ascribes to multiple methyl groups linked to the same carbon atom in the wavenumbers from 1500 cm^{-1} to 1000 cm^{-1}. The result is also well consistent with the high content of isoparaffins hydrocarbons in the product over the K-$ZnFe_2O_4$@K-ZSM-5 catalyst (Figure 3c).

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Figure 7. Optimized periodic structures of a H-ZMS-5, b Ce-ZSM-5 and c K-ZSM-5; C_2H_4 *(i)* , C_3H_6 *(ii)* and C_4H_8 *(iii)* are adsorbed on zeolite with adsorption energies (E_{ads}). The alkali metal bond with O in Si-O-Al.

With the introduction of zeolite, olefins generated on iron-based catalysts are further reacted to form long-chain hydrocarbons and aromatic hydrocarbons. To investigate the process mechanism, C_3H_6 was selected as probe reactant to detect dynamic changes on ZSM-5 by *in situ* DRIFT. As shown in the Figure 6c, 6d and Figure S16, the wavenumber in 3000 cm^{-1} is attributed to the double-bond telescopic vibration of the C=C of C_3H_6. For H-ZSM-5, three distinct infrared absorption peaks of benzene rings appear between 1500 cm^{-1} to 1200 cm^{-1}, which indicates that C_3H_6 has been aromatized over H-ZSM-5. When the H-ZSM-5 catalyst is located in a C_3H_6 atmosphere, the absorption peak belonging to C_3H_6 gradually decreases, and the absorption peak of the benzene ring gradually increases. As expected, the main olefins from $ZnFe_2O_4$catalyst are reacted at the acid site of ZSM-5 to produce more gasoline-range hydrocarbons, especially isomeric and aromatic compounds with high octane numbers. In terms of K-ZSM-5, there are other infrared absorption peaks between 1700-1500 cm^{-1} and 1000-900 cm^{-1}, which are attributed to alternatives to benzene or isomeric hydrocarbons. These evidences show that ZSM-5 treated with K ions can efficiently transform olefins to gasoline hydrocarbons (Figure 3, 6 and S16). Clearly, the regulation of the microenvironment of zeolite through ions exchange is conducive to the oriented generation of C_{5+} hydrocarbons.

In order to understand the intrinsic reason for the enhanced catalytic selectivity over an alkali metal (K and Ce) modified ZSM-5 catalyst, DFT calculations were performed to investigate the structure and electronic properties of the catalysts, as well as the adsorption of intermediates (C_2H_4, C_3H_6, and C_4H_8). As shown in Figure 7, the introduction of alkali metal does not affect the overall structure of the H-ZSM-5 catalyst, maintaining the MFI zeolite structure. It has been reported that after ions exchange in ZSM-5, ions often replace Al on the backbone to change its surface acidity.[18] By optimizing the individual ZSM-5 zeolite rings, the adsorption energy of C_nH_{2n} was calculated.

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Figure 8. Main reaction routes for CO_2hydrogenation over different composite catalysts.

The adsorption energy of C_2H_4, C_3H_6, and C_4H_8 was -0.10 eV, -0.31 eV and -0.39 eV, respectively, which are effective adsorption. The ZSM-5 structure with Ce and K modification was optimized, and the adsorption energy of olefins was calculated for the optimized structure. These detailed results were shown in Table S11 and S12. With the introduce of Ce and K into H-ZSM-5, the adsorption capacity of olefins on Ce-ZSM-5 and K-ZSM-5 is enhanced. It is worth noting that the Ce-ZSM-5 has strong adsorption of olefins. When metal ions bond with O, it has significantly enhanced adsorption behavior for C_4H_8 and stronger adsorption behavior for $C_3H_6$when it replaces Al (Figure S17). Strong adsorption and more acid sites lead to enhanced aromatization of olefins during the secondary reaction on Ce-ZSM-5. Combined with *in situ* DRIFT spectra of ZSM-5 (Figure 6 and S16), the main products of olefins are aromatic compounds over Ce-ZSM-5. Meanwhile, hydrocarbon formation in *in situ* DRIFT spectra of K-ZSM-5 is different from aromatic compounds. It explains that after the introduction of Ce, the ZSM-5 has a stronger adsorption behavior for olefins, which is conducive to aromatization and not conducive to isomerization, resulting in the formation of more aromatic compounds in the product (Figure 3c). The introduction of alkaline metal to regulate acidity changes the adsorption capacity of olefins intermediates over different ZSM-5 zeolites, which further affects olefins secondary reaction on ZSM-5 catalysts. As mentioned above, the microenvironment of H-ZSM-5 can be effectively regulated by alkali metal additives, which helps to achieve the guided synthesis of catalytic products. The reaction routes over different composites are also listed in Figure 8. For the conventional H-ZSM-5 catalyst, direct hydrogenation and aromatization of light olefins are mainly performed, exhibiting poor hydrocarbon selectivity. By contrary, olefins mianly occurs oligomerization and isomerization reaction over K-ZSM-5 zeolite, while it mainly occurs oligomerization and aromatization reaction over Ce-ZSM-5 zeolite.

4. Conclusion

In conclusion, we report an iron-based composite catalyst with a capsule structure, $ZnFe_2O_4$@ZSM-5. The catalyst has adjustable core-shell microenvironment, that is the microelectronic environment of the core catalyst is changed by the alkali promoters and the acid environment of the shell catalyst is changed by ions exchange, which yield of C_{5+} products reaches 60.1% g^{-1}, a record-breaking value among composite catalysts. Thereinto, CO_2 molecules are converted to CO through RWGS reaction, and then alkenes are synthesized by the FTS process over the $ZnFe_2O_4$ catalyst. Thereinto, long-chain olefins are synthesized over the K-$ZnFe_2O_4$. The formed olefins secondary reactions such as isomerization, oligomerization hydrogenation and aromatization reactions are initiated at the acid site of ZSM-5 shell. The strategy of alkali metal ions exchange weakens the strong acidic site of the zeolite and thus promotes the production of heavy gasoline products. Especially, the K ions, are effective in reduce the strong acids and precisely control the acidic sites of ZSM-5, which exhibits improved chemical adsorption capacity for different types of olefins intermediates as demonstrated by DFT calculation and *in situ*characterization. As a consequenece, when $ZnFe_2O_4$ is encapsulated into the K-ZSM-5 shell, it effectively enhances the mass transfer process of long-chain intermediate olefins and greatly improves the selectivity of gasoline products. This provides a way to improve the selectivity or yield of the target product over a tailor-made composite catalyst.

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Notes

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Present Addresses

+If an author's address is different than the one given in the affiliation line, this information may be included here.

Data Availability Statement

The authors declare that the data that supports the findings of this study are available in the supplementary material of this article. The numerical data for size distribution XRD, XPS spectra and XAFS in Figure 1 and* Figure 2, BET, In-situ DRIFTS, and DFT calculations in Figures 5, Figures 6 and Figure 7, and additional illustrative figures in the main text are provided in the supplementary information are provided as zip files in the supplemental material.

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Graphical Abstract

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The composite catalyst with tuned micro-environments of core-shell components exhibits ultra-high yield of gasoline hydrocarbons. Long-chain olefins intermediates from K-$ZnFe_2O_4$ core catalyst mainly occur oligomerization and isomerization reaction to obtain isoparaffin-rich hydrocarbon products over K-ZSM-5 shell catalysts, achieving CO_2 utilization upgrading.